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Magneto-structural Correlations in Chains of Bifolded $Cu_2Cl_6{}^{2-}$ Dimers

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Abstract

The magnetic susceptibility of two $ACuCl_3$ salts containing chains of bibridged $Cu_2Cl_6{}^{2-}$ dimers has been measured. Each copper ion bridges to a chloride in an adjacent dimer, thus assuming a 4 + 1 coordination geometry. Structurally, each dimer is characterized by a bridging Cu–Cl–Cu angle, ϕ, and a fold angle, σ, at each copper center. The high temperature susceptibility data for (4-benzylpiperidinium)$CuCl_3$ ($\phi = 95.3°$, $\sigma = 28.9°$) obey a Curie–Weiss law which has a positive intercept ($\theta = 13$ K), indicating a predominant ferromagnetic interaction. For the low temperature data, the Curie–Weiss plot has a negative intercept ($\theta' = -4$ K), showing that a net antiferromagnetic coupling exists. The data is interpreted quantitatively in terms of a system of ground state triplet dimers, with singlet–triplet energy splitting $\Delta E(=2J)$ of $\Delta E/k = 60$ K with interdimer interactions, accounted for with a mean field approximation of $J'/k = -3$ K. The salt (paraquat)Cu_2Cl_6 ($\phi = 97.5°$, $\sigma = 31.7°$) behaves as an antiferromagnetic alternating chain with $J/k = 19$ K and $J'/k = 2$ K. The magnetic properties of two other salts containing structurally similar chains, $(CH_3)_2NH_2CuCl_3$ and $(CH_3)_2CHNH_3CuCl_3$, have been reinvestigated using pulsed high field magnetization techniques. Comparison of these systems shows that, with ϕ constant, there is an approximate linear relationship between ΔE and the fold angle, σ. At $\phi = 95.5° \pm 0.3°$, the interaction is ferromagnetic for $\sigma > 22°$ and antiferromagnetic for smaller values of σ. These conclusions are confirmed by extended Hückel MO calculations for the intradimer interactions within the Hoffmann framework for exchange coupling.

Introduction

Compounds of the type $ACuCl_3$ frequently form salts containing clearly recognizable $Cu_2Cl_6{}^{2-}$ dimers [1]. In one class, the dimers form chains, with each copper ion bridging to a halide ion in an adjacent dimer, yielding an alternating chain. One arrangement in this class is illustrated in Fig. 1a for the compound $(C_6H_5C_5H_9NH_2)CuCl_3$ (henceforth (4-BzpipdH)-$CuCl_3$ where $(C_6H_5C_5H_9NH_2)^+$ is the 4-benzylpiperidinium cation, which has recently been synthesized by Pellacani and co-workers [2]. The stacking pattern of the dimers in the chain is shown schematically in Fig. 1b. Copper ions within a dimer are related by centers of inversion; adjacent copper ions between dimers are related by a two-fold axis. These chains and the geometry of the $Cu_2Cl_6{}^{2-}$ anions are very reminiscent of those found in $[(CH_3)_2NH_2]CuCl_3$ [3] (henceforth (DMA)$CuCl_3$]. Other salts in this class stack as shown in Fig. 1c. These include $(CH_3)_2$-$CHNH_3CuCl_3$ [4] ((IPA)$CuCl_3$)) and (paraquat)Cu_2-Cl_6 [5] ((PQT)Cu_2Cl_6). In these, adjacent dimers are related by a center of inversion. Because of the interest in magneto-structural correlations in transition metal clusters, we are undertaking a systematic study of the magnetic properties of a series of copper(II) halide salts. It is well documented that the exchange coupling, J, (defined by $\mathcal{H} = -2JS_1S_2$) depends linearly upon the Cu–O–Cu bond angle in a large series of copper(II) hydroxide systems [6]. What is not so clear, however, is how systems behave when more than one structural parameter is varied. In this paper, we report the magnetic susceptibility studies of (4-BzpipdH)$CuCl_3$ and (PQT)Cu_2Cl_6, as well as a reinvestigation of the magnetic properties of (DMA)$CuCl_3$ and (IPA)$CuCl_3$.

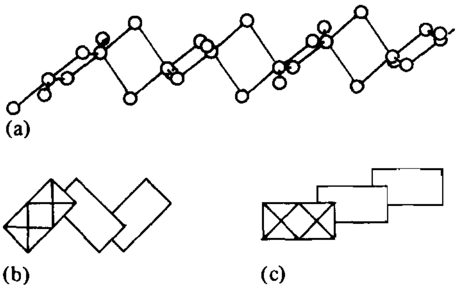

Fig. 1. (a) Chain of dimers in (4-BzpipdH)$_2Cu_2Cl_6$. (b) Stacking of dimers in (4-BzpipdH)$_2Cu_2Cl_6$. (c) Stacking of dimers in $(CH_3)_2CHNH_2CuCl_3$.

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TABLE I. Structural and Magnetic Parameters for $Cu_2Cl_6^{2-}$ Chains

	$KCuCl_3$ [a]	$(MEL)Cu_2Cl_6$ [b]	$(IPA)CuCl_3$ [c]	$(DMA)CuCl_3$ [d]	$(4\text{-}BzpipdH)CuCl_3$ [e]	$(Paraquat)Cu_2Cl_6$
$Cu–Cl_{basal}$(ave) (Å)	2.288	2.297	2.290	2.300	2.290	2.288
$Cu–Cl_{axial}$ (Å)	2.941, 3.113	2.730, 3.125	2.699	2.733	2.6687	2.668
Cu–Cu (Å)	3.443	3.376	3.417	3.444	3.415	3.48
trans Cl–Cu–Cl[a] (°)	175.8	175.5	175.10	176.0	177.5	172.5
trans Cl–Cu–Cl[b] (°)	173.2	171.3	160.53	156.0	151.0	148.3
Cu–Cl–Cu (sym), ϕ (°)	95.5	95.8	95.5	95.6	95.3	97.5
Cu–Cl–Cu (asym), ϕ' (°)	91.0–100.6	95.0	95.0	89.4	91.5	91.5, 94.0
σ	1.5	7.6	19.2	23.6	28.7	31.7
J/k (K)	−28	−28	−14	~15	30	−19
J'/k (K)		~7	~−8	~−13	−4	−2
ϕ'/r (°)		34.8	33.1	33.5	34.3	35.2
$\epsilon_s - \epsilon_a$ (eV)	0.1153	0.1140	0.1128	0.1018	0.0916	0.1111

[a] Ref. 17. [b] Ref. 18. [c] Ref. 4. [d] Refs. 3 and 14. [e] Ref. 2. [f] Ref. 5.

The relevant structural parameters of these four salts (along with two other salts, $KCuCl_3$ and melaminium Cu_2Cl_6) are summarized in Table I. Each copper ion has a 4 + 1 coordination geometry – four short Cu–Cl distances (~2.3 Å) defining a nonplanar basal geometry and a long Cu–Cl distance (~2.7 Å) defining an apical direction. The two *trans* Cl–Cu–Cl angles (θ) in the base are distinctly different – one is nearly linear ($\theta \sim 180°$); the other *trans* Cl–Cu–Cl bond angle is substantially bent ($\theta \sim 145°–160°$). The geometry is frequently described as intermediate between trigonal bipyramidal and square pyramidal. Indeed, this is so if only the basal region is examined. However, the apical Cu–Cl distance is substantially larger than that found for either the trigonal bipyramidal end member (2.4 Å) [7] or the square pyramidal end member (2.5 Å) [8]. Thus, this geometry, so characteristic of Cu^{2+} salts, represents one of the possible geometries obtained when one axial ligand is removed from the 4 + 2 coordination geometry found in $(RNH_3)_2CuCl_4$ salts [9].

Because of this C_{2v} distortion of the copper coordination sphere, the $Cu_2Cl_6^{2-}$ anions are nonplanar. We can characterize the nonplanarity by a fold angle, σ, between the bridging Cu_2Cl_2 plane and the terminal $CuCl_3$ plane, as shown in Fig. 2. In the four salts, the angle varies from 19.3° (IPA) to 31.7° (PQT). The fold is essentially along the linear Cl–Cu–Cl direction and leaves unperturbed the two chlorine atoms which lie on this axis. Thus, two of the lobes of the $d_{x^2-y^2}$ orbitals remain oriented directly towards these chlorine atoms. This is in contrast to the isolated $Cu_2Cl_6^{2-}$ dimers in $\phi_4AsCuCl_3$ [10a], ϕ_4PCuCl_3 [10b] and $\phi_4SbCuCl_3$ [10c], where a D_{2d} distortion involving a symmetric twist (twist angle τ) occurs with the twist axis along the Cu–Cu direction. In this case, all chlorine atoms

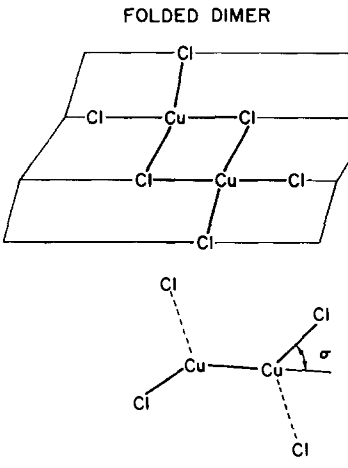

Fig. 2. Idealized geometries of bifolded dimers. Top: perspective view. Bottom: edge view showing location of Cl^- ions from adjacent dimers.

are moved out of the local xy plane, so that the lobes of the $d_{x^2-y^2}$ orbital no longer point directly towards any of the chlorine atoms.

Finally, we note that the intradimer bridging geometry remains nearly invariant in most of the salts being compared. The symmetric Cu–Cl–Cu bridging angles are 95.51°, 95.6°, and 95.3° for the IPA, DMA and 4-BzpipdH salts, for example, but is substantially larger (97.5°) for the PQT salt. We note also that the asymmetric interdimer bridging geometry changes although the apical Cu–Cl distance remains nearly unchanged. This variation will complicate the interpretation of the magnetic data, but these interactions are generally weaker than the corresponding interdimer interaction.

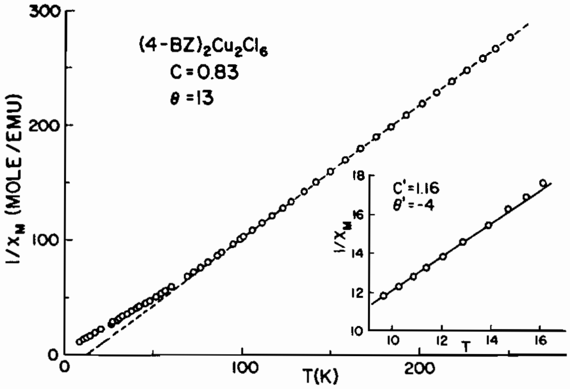

Fig. 3. Plot of $1/\chi_m$ *vs.* T for $(4\text{-BzpipdH})_2Cu_2Cl_6$ showing the high temperature and low temperature (inset) linear regions.

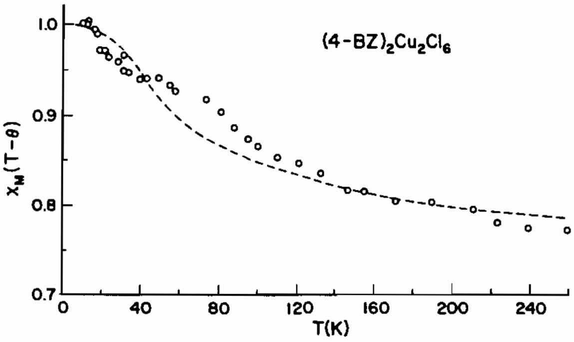

Fig. 4. Plot of $\chi_m(T-\theta')/C'$ *vs.* T for $(4\text{-BzpipdH})_2Cu_2Cl_6$.

Magnetic Measurements

The magnetic susceptibility data were collected with a P.A.R. vibrating sample magnetometer with a Janis cryostat over the temperature range from the liquid He temperature to 300 K. Temperature was measured with a germanium resistance thermometer or a copper-constantan thermocouple calibrated against potassium chrome alum and $HgCo(SCN)_4$ [11]. Data was corrected for diamagnetism and temperature independent paramagnetism (60×10^{-6} emu/mol). The pulsed high field magnetization studies reported were undertaken at the Kamerlingh-Onnes Laboratorium, Leiden.

$(C_6H_5C_5H_9NH_2)CuCl_3$

For $(4\text{-BzpipdH})CuCl_3$, samples obtained from our own laboratory as well as from Prof. Pellacani's laboratory were utilized. All samples exhibited identical behavior. However, virgin samples exhibited a different behavior to samples which had been previously cooled to cryogenic temperatures. It is the data for the virgin samples which are reported. The magnetic susceptibility, reported per mole of $Cu_2Cl_6^{2-}$ anions, increased as the temperature was lowered, indicating the absence of any strong antiferromagnetic coupling. The $1/\chi_m$ *versus* T plot (Fig. 3) confirms this conclusion. Two linear regions are observed. At high temperatures, the Curie–Weiss region [$\chi_m = C/(T-\theta)$] is characterized by $C = 0.83$ and $\theta = 13$ K. The value of C corresponds to $g = 2.104$. The positive intercept shows that the predominant exchange coupling is ferromagnetic in nature. Based on the structural characteristics, we can assume that the triplet state is low in the $Cu_2Cl_6^{2-}$ dimers. At low temperatures, another linear region is found (inset, Fig. 3). The Curie–Weiss constants are $C' = 1.16$ and $\theta' = -4.0$. This gives $g = 2.154$ for the triplet state. The negative value of θ' corresponds to an antiferromagnetic coupling of the triplet ground states and it is equivalent to an exchange coupling for the asymmetric bridge of $J'/k = 3$ K. This value of J' has been confirmed by a magnetization study [12].

Detailed analysis of the data can proceed in several ways. Blöte has reported on numerical calculations on the alternating Heisenberg chain [13a] and a Pàde approximate fit to earlier results has been given [13b]. We have obtained an analytical solution for a chain of Ising coupled Heisenberg dimers [14a]. However, since we have a system with $2J' \ll \Delta E \sim kT$, the mean field expression [14b]

$$\chi_m = [C'/(T-\theta')]\{3/[3+\exp(\Delta E/kT)]\} \qquad (1)$$

is appropriate. If this is valid, a plot of $\chi_m(T-\theta')/C'$ *versus* T should give simply a plot of the Boltzman factor for the population of the triplet state. Indeed, this is observed, as shown in Fig. 4, within a scatter of ±2% except for a systematic mismatch just above liquid nitrogen temperature probably due to a small miscalibration of the thermocouple at those temperatures (χT plots magnify these errors). Analysis of the data yields $\Delta E/k = 60$ K for $C' = 1.15$ ($g = 2.145$). It should be noted that ΔE is extremely sensitive to the value of C', a 2% change in C' inducing a 35% change in ΔE. The high temperature Curie–Weiss constant of $\theta = 13$ K corresponds to $\Delta E/k = 36$ K.

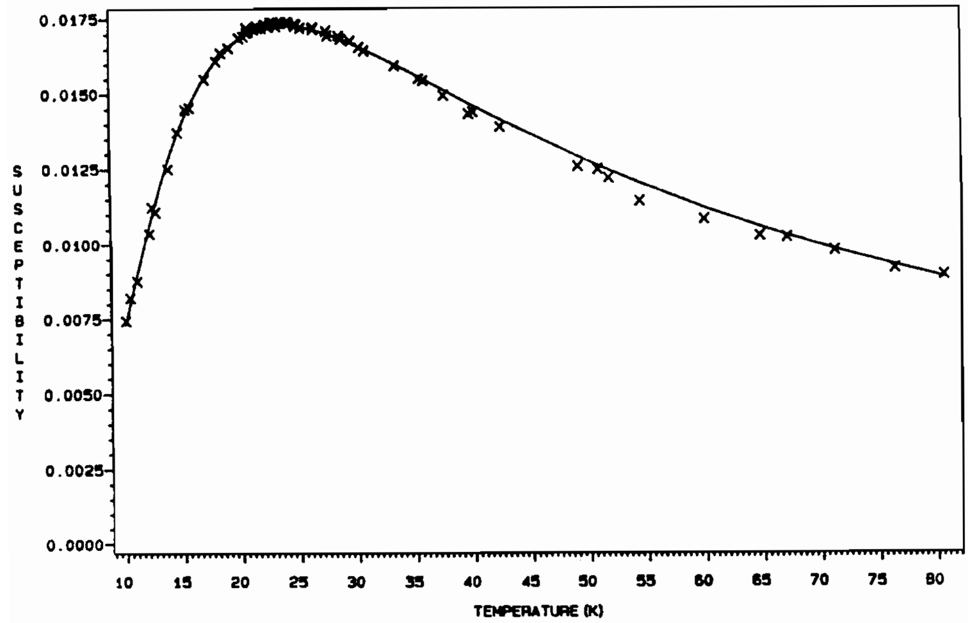

Fig. 5. Plot of χ_m *vs.* T for (paraquat)Cu_2Cl_6. Solid curve: alternating antiferromagnetic chain with J/k = 19.0 K, J'/k = 1.7 K.

(Paraquat)Cu_2Cl_6

The salt was prepared by mixing stoichiometric amounts of paraquat and $CuCl_2 \cdot 2H_2O$ in dilute HCl, and crystallized by slow evaporation [5].

The salt behaves as a typical alternating antiferromagnetic chain with χ reaching a maximum at 22 K. Evidence for a small amount of 'impurity' spins, probably due to lattice defects, is seen at very low temperatures. Otherwise, it is clear that extrapolation of the χ curve in the 6–20 K region will yield $\chi = 0$ at $T = 0$, confirming the alternating chain supposition. The fit to the Heisenberg alternating chain model [15] yields $J/k = -19.0(2)$ K, $J'/k = 2(1)$ K with $g = 2.12$ (fixed). This is shown by the solid line in Fig. 5. It should be noted that the value of J is quite accurately determined, being fixed by the temperature at which χ reaches a maximum. On the other hand, J' is strongly coupled to the value of g and so is much less reliable.

[$(CH_3)_2CHNH_3$]$CuCl_3$

Initially, our powder susceptibility data on this salt were interpreted with an alternating Ising chain model to yield approximate exchange values for J/k and J'/k [4]. A recent investigation has used the alternating Heisenberg antiferromagnetic chain model to obtain the more accurate values of $J/k = -14$ K and $J'/k = -5$ K [15]. In this paper measurement of the high field magnetization *versus* field was made for powdered samples $IPACuCl_3$ (see ref. 12 for reference to the experimental details). The results, shown in Fig. 6, are characteristic of an alternating antiferromagnetic chain. The moment is essentially zero up to 10 T and reaches its expected saturation value at 40 T (the limit of the instrumentation). From the susceptibility studies, it is known that the susceptibility reaches a maximum at 17 K, which requires $J/k = -14$ K, since $\chi_{max} \sim 1.2\ J/k$ for an alternating chain, essentially independent of α. The low field magnetization data give good agreement with the theoretical curve for an alternating chain with $\alpha = J'/J = 0.6$. However, the high field data show significant deviations from the theoretical curve. These can be accounted for by interchain interactions which may be modeled via a mean field model approximation ($H_{eff} = H_o + \lambda M$; $\lambda = \theta/C$), and yields J/k = 14 K, α = 0.6, and θ = 1 K, where θ is the mean field interchain interaction. Thus we conclude that within the chain, $J/k = -14$ K and $J'/k = -8.4$ K.

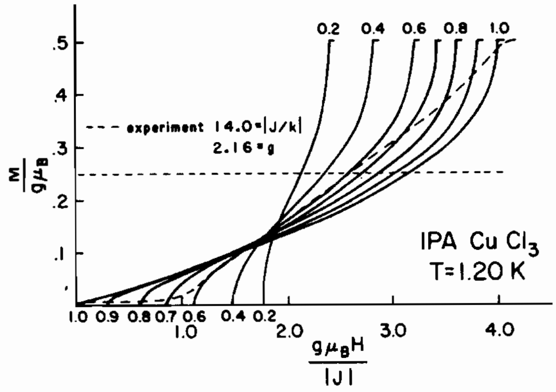

Fig. 6. Plot of reduced magnetization *vs.* reduced field for $IPACuCl_3$ at 1.2 K. Dashed curve: experimental results. Solid lines: theoretical curves for various values of the alternation parameter α.

$[(CH_3)_2NH_2]CuCl_3$

For this salt (DMA)$CuCl_3$, an ac [zero field] susceptibility study had previously been reported [14a]. Powder samples exhibited net antiferromagnetic behavior, with a Curie–Weiss constant of $\theta = -0.4$ K. Various one-dimensional models were used to fit the data, all utilizing antiferromagnetic intra- and interdimer exchange interactions. It was concluded that both interactions were of the order of 0 to –2 K.

The results of the present high field pulsed magnetization measurements on powder samples at 1.2 K are shown in Fig. 7. These results are definitely not characteristic of a simple alternating antiferromagnetic chain. Rather, the curve exhibits behavior typical of a three dimensionally ordered system with hidden canting. This can be visualized by averaging the typical single crystal results for a canted metamagnet [16] to obtain the curve for a powdered sample. Then, the first linear portion corresponds to the decoupling of a weak antiferromagnetic interaction (presumably between chains). The second linear portion corresponds to the alignment of a canted spin system under the influence of the external field, as evidenced by the fact it extrapolates to a non-zero magnetization value at $H = 0$. Saturation occurs above 16 T. The magnetization results at 4.2 K show no evidence of three-dimensional ordering. Since the zero field susceptibility data [14a] show no evidence of ordering down to 2 K, it is concluded that magnetic ordering occurs in the regime between 1.2 and 2 K.

These data supply immediate information concerning the nature of the exchange interactions within the chains. Since the copper atoms within each dimer are related by a center of inversion in the paramagnetic region, the exchange interaction within the dimer must be ferromagnetic. (An antiferromagnetic intradimer interaction would lead directly to co-linear spin alignment, in contradiction to the observed canting.) Furthermore, any interchain interactions must be of such a nature that spins on atoms related by the body centering operation are antiferromagnetically coupled to account for the initial rapid rise in magnetization.

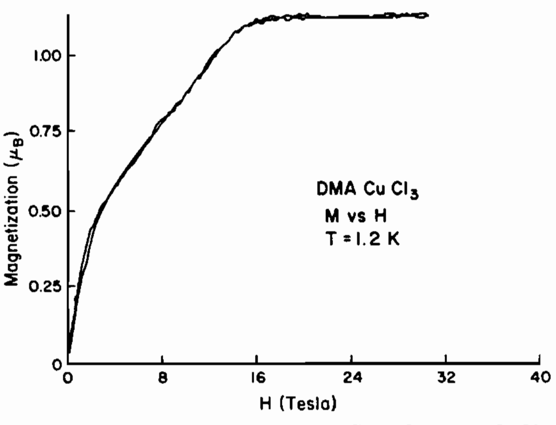

Fig. 7. Plot of magnetization *vs.* field for $DMACuCl_3$ at 1.2 K.

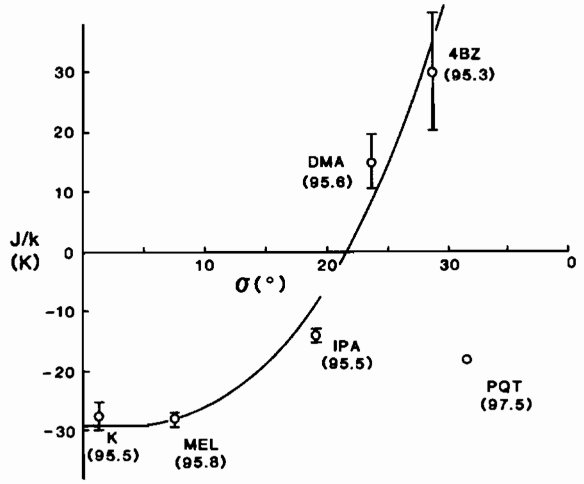

Fig. 8. Plot of exchange energy, J/k *vs.* distortion angle for several $Cu_2Cl_6^{2-}$ dimer systems.

Quantitative analysis of the full curve cannot be made since theoretical results for an alternating chain with spin canting are not available. Nevertheless, estimates of J, the intradimer interaction, J', the interdimer interaction, and J_{ic}, the interchain coupling, can be made. The magnitude of the interchain couplings can be estimated from the magnitude of the field at the 'knee' in the curve, $H_1 = 2$ T to yield $J_{ic}/k = -2$ K. Information concerning the strength of total antiferromagnetic interaction (J_{AF}) can be obtained from the H_{sat}, the field at which the magnetization saturates. The energy difference between ground state and the spin state in the saturation field is

$$g\mu_\beta H_{sat} = N/2(-2J_{AF})S(S+1).$$

From the value of $H_{sat} = 15$ T, we obtain $J_{AF}/k \simeq -15$ K. Since $J_{AF} = J' + J_{ic}$, we have $J'/k \simeq -13$ K. The previous susceptibility study then requires that the ferromagnetic interdimer coupling, J, must be nearly equal to the J_{AF} deduced from the magnetization experiments. Thus we conclude that $J/k \simeq 15$ K.

Magneto-structural Correlations

In light of the above data, it is worthwhile examining magneto-structural correlations in a series of symmetrically bibridged $Cu_2Cl_6^{2-}$ anions. The data is represented graphically in Fig. 8. In addition to the salts with bifolded dimers, two salts with planar dimers ($KCuCl_3$ [17] and (melaminium)Cu_2Cl_6) [18]

are included*. There is a relationship between the extent of distortion and the copper coordination number. The planar, nearly undistorted, dimer in $KCuCl_3$ has a 4 + 2 coordination; the bifolded dimers have a 4 + 1 coordination, the dimers in the melaminium salt have an intermediate 4 + 1 + 1′ coordination. For comparison purposes, the bridging Cu–Cl–Cu angles are included in parenthesis. For the salts with $\phi = 95.5° \pm 0.3°$, a general correlation of J with σ is observed. This is represented by the solid line in Fig. 8, drawn as an aid to the eye only. The curve must approach $\sigma = 0$ horizontally since the σ distortion is symmetric about this geometry. At larger values of σ, J must reach a maximum (at the value where $\epsilon_s = \epsilon_a$ in Hoffmann's formalism, see below). For (PQT) Cu_2Cl_6, the bridging angle is substantially larger (~2°) and the exchange is expected to become more antiferromagnetic. This is precisely the behavior observed.

The theoretical framework for making magneto-structural correlations has been given by Hay *et al.* [20], in which the singlet–triplet energy separation, ΔE or $2J$, is expressed in terms of quantum mechanical exchange and coulomb integrals and the one-electron molecular orbital energies. This leads to an expression of the type

$$\Delta E = 2J = 2J_F - A(\epsilon_s - \epsilon_a)^2 = 2J_F - 2J_{AF}$$

where $J_F > 0$ is the ferromagnetic contribution to ΔE and the last term, where ϵ_s and ϵ_a are the energies of the symmetric and antisymmetric combination of magnetic orbitals, gives the antiferromagnetic contribution. It is assumed that the primary effect of a structural change will be on ϵ_s and ϵ_a, and that the other terms will be essentially structure independent. Calculations were carried out by Hay *et al.* [20] as well as Bencini and Gatteschi [21] for a series of distortions. Results of these calculations show, for example, that $|\epsilon_s - \epsilon_a|$ increases as the bridging Cu–L–Cu angle, ϕ, increases when $\phi > 90°$, in accord with the experimental observation of increasing antiferromagnetic character as ϕ is increased. For the twisted dimer, they also show that $\epsilon_s = \epsilon_a$ at an intermediate value of the twist angle, τ. Thus as τ increases from $\tau = 0$, the interaction is predicted to become more ferromagnetic before reaching some maximum value and decreasing as $\tau \to 90°$. Evidence for this turnover has been seen in a copper–bromide system [22]. It was thus decided to perform similar calculations for the bifolded dimers.

For the bifolded dimer, we have evaluated $(\epsilon_s - \epsilon_a)$ in the extended Hückel framework [23]. The computational procedures are detailed in Appendix 2 of ref. 23. The atomic orbital energies were assumed to be the same throughout the series and no self-consistent charge iterations were done in each case either on the monomer or on the dimeric units. Double-zeta Roothan–Hartree–Fock atomic wavefunctions were used for all atoms and the exponents of the basis functions and the coefficients were taken from the tables compiled by Clementi and Roetti [24]. Actual geometries were utilized. The results (Table I) are in excellent agreement with the experimental results, with $\Delta\epsilon^2 = (\epsilon_s - \epsilon_a)^2$ largest for the antiferromagnetic system and progressively smaller as the interaction becomes less antiferromagnetic. No crossover from $\epsilon_a < \epsilon_s$ to $\epsilon_a > \epsilon_s$ was found for these geometries.

The J' values should also be commented upon. It has been proposed that J' depends upon the ratio ϕ'/R where ϕ' is the asymmetrical Cu–Cl–Cu bridging angle and R is the long (axial) Cu–Cl distance [9]. A smooth relationship between J' and ϕ'/R has been observed for a series of salts, mostly chains of the type $CuCl_2L_2$ in which the coordination geometry is planar. However, our data does not fall on that curve. This is not surprising, since our coordination geometry is much distorted.

This study thus verifies that an increase bifold angle, for $\sigma < 32°$, leads to an increasingly ferromagnetic exchange interaction. It also highlights the need for more magnetic and structural data on copper halide oligomers and chains so that the full range of magneto-structural correlations can be clearly delineated.

Acknowledgements

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*Another planar dimer, in $LiCuCl_3 \cdot 2H_2O$, has been investigated [15] and interpreted in terms of an alternating chain with $J = -4$ cm^{-1} and $\alpha = 0.9$. However, the salt orders three dimensionally at 4.8 K, so it is clear that a simple one dimensional model is not appropriate. An earlier investigation [19] identified two exchange pathways in addition to the intra- and interdimer pathways with $|J/k| \sim 15-25$ K for all pathways. Unfortunately, they identified the intradimer coupling as ferromagnetic (J/k = 22 K). With a bridging angle of $\phi = 95.1°$, this clearly is not reasonable in light of the known magneto-structural relationship between J and ϕ. An antiferromagnetic coupling of that magnitude would be reasonable, however.

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